

## Description

# METHOD FOR APPLYING A LAYER TO A HYDROPHOBIC SURFACE

### BACKGROUND OF INVENTION

[0001] FIELD OF THE INVENTION

[0002] The present invention relates to the field of applying layers of material to hydrophobic surfaces; more specifically, it relates to method for reducing the quantity of the material applied to a substrate having a hydrophobic surface in order to form a uniform layer of the material on the hydrophobic surface.

[0003] BACKGROUND OF THE INVENTION

[0004] There are many aqueous based materials that must be applied to surfaces that are hydrophobic or water repelling surfaces. In order to form a uniform coating, especially by spinning or spin coating, an excess of the aqueous based material must be applied, and the excess then removed and discarded. Since in many applications, for example, in

the application of a top anti-reflective coating (TARC) to a photoresist layer formed on a semiconductor substrate or wafer, the amount of discarded material is very many times the amount of material in the finished coating and thus the wastage and resultant cost is very high. Therefore, there is a need for a method to reduce the amount of material required to form a uniform layer on a hydrophobic surface.

#### **SUMMARY OF INVENTION**

[0005] A first aspect of the present invention is a method of forming a coating, comprising: (a) providing a substrate having surface; (b) forming a layer of water on the surface; and (c) forming a layer of a material on the layer of water.

[0006] A second aspect of the present invention is a method of forming an anti-reflective coating on a top surface of a photoresist layer, comprising in the order recited: (a) providing a substrate; (b) forming the layer of photoresist on the substrate; (c) spinning a layer of water on the top surface of the photoresist layer; and (d) spinning a layer of anti-reflective material on the layer of water to form the anti-reflective coating on the surface.

[0007] A third aspect of the present invention is a method of forming an anti-reflective coating on a top surface of a

photoresist layer, comprising in the order recited: (a) providing a semiconductor substrate; (b) forming the layer of photoresist on the substrate; (c) spinning a uniform layer of water on the top surface of the photoresist layer; and (d) spinning a layer of anti-reflective material on the layer of water to form the anti-reflective coating on the surface.

#### **BRIEF DESCRIPTION OF DRAWINGS**

- [0008] The features of the invention are set forth in the appended claims. The invention itself, however, will be best understood by reference to the following detailed description of an illustrative embodiment when read in conjunction with the accompanying drawings, wherein:
- [0009] FIGs. 1A through 1D are partial cross-sectional drawing illustrating application of the present invention to a photo-lithographic process according to the present invention;
- [0010] FIGs. 2A through 2D are schematic diagrams illustrating a method of forming a uniform layer on a hydrophobic surface according to the present invention;
- [0011] FIG. 3 is a flowchart of a method of applying a layer to a hydrophobic surface according to a control method;
- [0012] FIG. 4 is a flowchart of a method of applying a layer to a hydrophobic surface according to the present invention;

- [0013] FIG. 5 is a chart illustrating thickness of a TARC layer applied to hydrophobic surface versus the volume of TARC used to form the layer according to the control method of FIG. 3;
- [0014] FIG. 6 is a chart illustrating thickness of a TARC layer applied to hydrophobic surface versus the volume of TARC used to form the layer according to the method of the present invention of FIG. 4;
- [0015] FIG. 7 is a chart, illustrating image size control versus the volume of TARC applied according to the method of the present invention; and
- [0016] FIG. 8 is a chart comparing the control method and the method of the present invention to of resist thickness versus the size of subsequently printed and developed images.

#### **DETAILED DESCRIPTION**

- [0017] For the purposes of the present invention the terms layer and coating may be used interchangeably. A substrate may have any shape, including square, round, rectangular or irregular. Substrate may comprise almost any material, including but not limited to metal, plastic and glass. A wafer is a substrate having the geometry of a thin disk. When preferenced by the word "semiconductor" the terms

substrate and wafer imply the wafer or substrate comprises semiconductor materials such as silicon and/or germanium including bulk silicon wafers and silicon-on-oxide (SOI) wafers. Unless otherwise noted, the water used describing in the present invention is de-ionized (DI) water having resistivity of about  $10^{18}$  megohms or higher to avoid ionic and particulate contamination of the wafer. Any other purified water, such as distilled or water produced by reverse osmosis may be used. Where ionic contamination is not a concern, substantial amount of impurities may be present provided they do not adversely effect the operation of the present invention. The terms resist and photoresist are used interchangeably.

[0018] The present invention will be primarily described in the context of the semiconductor industry in general and in application of TARCs to photoresist layers in particular but is applicable to any product or process requiring coating a hydrophobic surface. An anti-reflective layer suppresses thin film interference effects by reducing the amount of energy reflected back into the photoresist layer from the photoresist/anti-reflective coating interface. Both the index of refraction and thickness of the anti-reflective layer are critical parameters in achieving optimal thin film in-

interference suppression. A TARC is therefore an antireflective coating applied to the top surface of the photoresist layer. Examples of photoresist materials are given in TABLE I and of TARC materials in TABLE II, but the invention should not be construed as limited to the particular photoresist or TARC materials listed in TABLES I and II.

[0019] The application of the present invention to the semiconductor industry should thus be considered as a primary example of the problem of coating hydrophobic surfaces.

[0020] FIGs. 1A through 1D are partial cross-sectional drawing illustrating application of the present invention to a photolithographic process according to the present invention. In FIG. 1A, a photoresist layer 100 having a top surface 105 has been formed on the top surface 110 of a substrate 115. Top surface 105 is a hydrophobic surface, which is not unexpected based on the chemical composition of modern photoresists (see TABLE I *infra*) since most photoresists are solvent based hydrophobic monomers, polymers or resins. The degree of hydrophobicity of a surface is measured by its water contact angle. Water contact angle is discussed *infra* more fully in reference to FIG. 2B. In FIG. 1B a water layer 120 having a top surface 125 has been formed on top surface 110 of photoresist layer 100.

In step 1C, a TARC layer 130 has been formed on top surface 125 of water layer 120. It is possible, in light of the chemical composition of TARC layer 130, being a small amount of water soluble polymer dissolved in water (see TABLE II *infra*), that water layer 120 is absorbed into TARC layer 130 although the water layer and TARC layer are shown as separate in FIGs. 1C. The lifetime of water layer 120 is very short under normal clean room conditions of about 20°C and about 38% to 40% relative humidity, being about less than a few seconds, so TARC layer 130 must be formed within a limited amount of time after formation of water layer 120. In FIG. 1D, photoresist layer 100 has been patterned by exposure to ultraviolet light and developed thus exposing top surface 110 of substrate 115 where the photoresist layer has been developed away. The developing process removes TARC layer 130 and water layer 120.

[0021] TABLE I is a list of exemplary photoresist materials suitable for use in the present invention when applied to semiconductor fabrication. Mid-ultraviolet (MUV) indicates a photoresist suitable for exposure at mid-ultraviolet wavelengths of light of about 365 nm. Deep-ultraviolet (DUV) indicates a photoresist suitable for exposure at

deep-ultraviolet wavelengths of light of about 248 nm or less. Other photoresists may be used as well.

[0022]

TABLE I

TYPE	MANUFACTURER	NAME	COMPOSITION
MUV	TOK OHKA KOGYO CO., LTD Kawasaki City, Japan	TSMR-iN011 PM TSMR-iN027 PM	Propylene glycol monomethyl ether acetate (60-95%) Polyhydroxy styrene type resin (5- 35%) Photoacid generator (<5%) Crosslinking agent (<5%)
		THMR-iP3250 LB	Ethyl lactate (61-79%) n-Butyl acetate (6-9%) Novolac resin (10-25%) Photoactive compound (2-8%)
	Sumitomo Chemical Co., LTD Osaka, Japan	Sumiresist PFI-58	Methyl amyl ketone(2-Heptanone) (63-88%) Novolac resin (8-25%) Photoactive compound (4-12%)
DUV	JSR Microelectronics Inc. Tokyo, Japan	JSR ARF AR 237J	Poly(meth)acrylate (5-25%) Alicyclic carboxylic ester (0-5%) Photoacid generator (0.1-3%) Propylene glycol monomethyl ether acetate (60-95%) Gamma-Butyrolactone (0-10%)
		JSR ARF AR 1570J	Poly(meth)acrylate (5-25%) Alicyclic carboxylic ester (0-10%) Photoacid generator (0.1-3%) Propylene glycol monomethyl ether acetate (75-85%) Gamma-Butyrolactone (0-10%)
		JSR KRF M20G	Polyhydroxy styrene derivative (10-30%) Iodonium salt compound (0.1-1%) Ethyl lactate (50-70%) Ethyl 3-ethoxypropionate (20- 30%)
	Rohm and Haas Electronic Materials LLC Marlborough, MA, USA	UV(TM) 110-0.4	Ethyl lactate (>70%) Aromatic Sulfur Compound (<2%) Aromatic Acrylic Polymer (<30%) Nonionic surfactant (<1%)
		UVII(TM) HS-0.8	Ethyl lactate (75-88%) Acrylic Copolymer (10-20%) Organic Siloxane Surfactant (0- 1%) Aromatic Sulfur Compound (0.1- 1%)

[0023] TABLE II is a list of exemplary TARC materials suitable for use in the present invention when applied to semiconductor fabrication. MUV indicates a TARC suitable for coating a photoresist exposed with mid-ultraviolet wavelength



light. DUV indicates a TARC suitable for coating a photoresist exposed with deep-ultraviolet wavelength light. Other TARC materials may be used as well.

TABLE II

TYPE	MANUFACTURER	NAME	COMPOSITION
MUV	Clariant Corporation Somerville, NJ, USA	AZ Aquatar	Fluoroalkyl acid ammonium salt (3%) 2-propenoic acid homopolymer (1.5%) Water (95.5%)
DUV	JSR Microelectronics Inc. Tokyo, Japan	JSR NFC 540	Fluoro acrylic polymer (1-10%) Anionic surfactant (0.1-1%) Water (90-99%)

[0024] As may be seen in Table II from the composition of AZ Aquatar be about 95.5% and JSR NFC 540 being about 90–99% water, TARC materials comprise substantial amounts of water.

[0025] FIGs. 2A through 2D are schematic diagrams illustrating a method of forming a uniform layer on a hydrophobic surface according to the present invention. In FIG. 2A, a semiconductor wafer 150 is positioned on top surface 155 of a wafer chuck 160. Semiconductor wafer 150 has, for example, a diameter of 100, 125, 200 or 300mm. A layer of photoresist 165 has been formed on a top surface 170 of semiconductor wafer 150. Wafer chuck 160 is rotatable about an axis 175 that is ideally perpendicular to top surface 155 of wafer chuck 160. Ideally axis 175 also passes through the geometric center 180 of wafer chuck 160 and

the geometric center 185 of semiconductor wafer.

[0026] In FIG. 2B, an application head 200 has a first nozzle 205 for applying water and a second nozzle 210 for applying TARC. Application head can move laterally in order to align either first nozzle 205 or second nozzle 210 with axis 175 so the material dispensed from the nozzles is ideally dispensed in the center of wafer 150. In FIG. 2B, first nozzle 205 is aligned with axis 175 and a predetermined amount of water sufficient to form a globule of water 215 on a top surface 220 of photoresist layer 165 is dispensed. Since top surface 220 of photoresist layer may not be level (as measured by a spirit level for example) and nozzle 205 may not be exactly centered on axis 175, wafer chuck 160 is rotated at a predetermined speed before and during the water dispense cycle. In one example, wafer chuck is rotated from about 5 to 50 rpm and about 2 to 20 ml of water are dispensed at a rate of about 0.5 to 3.0 ml/sec. The exact amount of water dispensed must not exceed an amount that would cause water globule 215 to collapse and not be less than an amount that will not subsequently spread evenly over the entire top surface 220 of photoresist layer 165. The exact speed of rotation of wafer chuck 160 must not exceed a speed of rotation

that would cause globule of water 215 to break apart.

[0027] It will be seen that globule of water 215 contacts top surface 220 of photoresist layer along a line 225 tangent to the surface 230 of the globule of water. A water contact angle  $\theta$ , is thus defined as the angle between a plane tangent to surface 230 of water globule 215 and top surface 220 of photoresist layer 165, at any point along their line of contact. The higher the water contact angle, the less wettable (more hydrophobic) the surface. The photoresists in Table I when spin coated on a substrate have top surfaces having water contact angles in the range of about  $40^{\circ}$  to  $60^{\circ}$ .

[0028] The phenomenon of wetting (hydrophilicity) or non-wetting (hydrophobicity) of a surface by a liquid (water) is measured by the liquid (water) contact angle. Contact angle measurement methods have been developed extensively over the past four decades and are well known in the art. A large body of reliable data and literature exists correlating contact angle data with the properties of surface tension.

[0029] In FIG. 2C, a water layer 235 is formed on top surface 220 of photoresist layer 165 by ramping up rotation of wafer chuck 160 after the predetermined volume of water has

been dispensed at a ramp rate of about 10,000 rpm/sec to a water spin off speed of about 500 to 2000 rpm and spinning for a spin off time of about 0.3 to 5.0 seconds. Simultaneously, second nozzle 210 of dispense head 200 is moved to align with axis 175. Water globule 215 (see FIG. 2B) is thus spread out to form water layer 235 and excess water spun off. Formation of water layer 235 is observable by formation of interference fringes during the spinning. Because water layer 235 will completely vaporize within a few seconds, it is difficult to determine the exact thickness of the water layer.

[0030] In FIG. 2D, a layer of TARC 240 is formed on a top surface 245 of water layer 235 by ramping up the rotation speed of wafer chuck 160 by about 10,000 rpm/sec from the spin-off speed to a TARC apply speed of about 2000–5,000 rpm within about 0 to 2 seconds of the spin off time for forming water layer 235 expiring, dispensing TARC at a rate of about 1.0 ml of TARC/sec for a predetermined amount of time (the time is a function of the total volume of TARC to be applied) and then ramping down the rotation speed of wafer chuck 160 by about –1,000 rpm/sec from the TARC apply speed to a casting speed of about 2,500 rpm and spinning at the casting speed for

about 15 seconds.

[0031] Water layer 235 may be only one to several molecular layers thick (or may not even be a continuous layer). Water layer 235 may even be no more than a collection of water molecules temporarily bound to the surface molecules of photoresist layer 165. Water layer 235 may be immediately absorbed into TARC layer 240 as soon as the TARC layer forms. It has been experimentally determined that the amount of TARC dispensed and still have a TARC layer of fixed thickness and uniformity is reduced by the spin application of water before application of TARC. It is believed that this reduction in TARC dispense volume is possible because water layer 235 alters the surface tension characteristics of the photoresist/TARC system and allows better wetting of photoresist layer 165 by TARC layer 240.

[0032] Consider a drop of a liquid resting on a solid surface. The drop of liquid may be considered as resting in equilibrium by balance the three forces involved, namely, the interfacial tensions between solid and liquid, between solid and vapor and between liquid and vapor. The surface tension of the solid will favor spreading of the liquid, but this is opposed by the solid-liquid interfacial tension and the

vector of the surface tension of the liquid in the plane of the solid surface. In the present invention, it is believed that the water layer increases the surface tension of the surface to be coated (photoresist surface), decreases the solid-liquid interfacial tension between the liquid (TARC) and surface being coated (photoresist surface), decreases the surface tension of the material being coated (TARC) or a combination of the forgoing effects.

[0033] The most important consideration for our purposes is that surface tension values are intimately related to the surface constitution. Even small changes in the outermost atomic layer of the photoresist are reflected in a change of surface tension and thus wettability (degree of hydrophilicity or hydrophobicity) of the photoresist.

[0034] In order to establish the reduction in volume of TARC required to coat a wafer to a fixed thickness and still have acceptable thickness uniformity across a wafer, from wafer to wafer and from tool to tool a set of experiments were performed against a control process. The control process and experimental process are illustrated in FIGs. 3 and 4 respectively and described *infra*. The photoresist and TARC materials were selected from TABLE I and TABLE II respectively. Wafers were 200 mm diameter semicon-

ductor wafers.

[0035] FIG. 3 is a flowchart of a method of applying a layer to a hydrophobic surface according to a control method. In step 300, a layer of photoresist is applied. The photoresist layer is pre-baked to drive out excess solvent and cooled to room temperature. In step 305, a volume of TARC at about 1ml/sec is applied at 0 rpm spin speed. The volume of TARC varies by experimental cell and is discussed *infra*. In a nominal case the volume of TARC dispensed is about 5 ml. Then, in step 310, the wafer is ramped up to a casting speed of about 2,500 rpm at a ramp rate of 1,000 rpm/sec and spun for about 15 seconds to spin off excess TARC. The wafer rotation is then stopped.

[0036] FIG. 4 is a flowchart of a method of applying a layer to a hydrophobic surface according to the present invention. In step 350, a layer of photoresist is applied. The photoresist layer is pre-baked to drive out excess solvent and cooled to room temperature. In step 355, the wafer is rotated at about 15 rpm and about 10 ml of water is dispensed at a rate of about 0.65 ml/sec. In step, 360, as soon as the water dispense is completed, the wafer is ramped from about 15 rpm to about 1,000 rpm at a ramp rate of about 10,000 rpm/sec and spun for a total time of about 0.3

seconds. In step 365, the wafer is ramped from about 1,000 rpm to about 3,500 rpm at a ramp rate of about 10,000 rpm/sec and a volume of TARC at about 1ml/sec is applied. The volume of TARC varies by experimental cell and is discussed *infra*. In a nominal case the volume of TARC dispensed is about 0.3 ml. There is now an option. The method can proceed to step 370A or 370B. In step 370A, the wafer rotation is ramped down to a casting speed of about 2,500 rpm at a rate of about -1,000 rpm/sec and allowed to spin for about 15 seconds. The wafer rotation is then stopped. In step 370B, The wafer rotation is ramped down to about 150 rpm at a ramp rate of about -50,000 rpm/sec and held at about 150 rpm for about 1 second. Then the wafer the wafer rotation is ramped up to a casting speed of about 2,500 rpm at a rate of about 1,000 rpm/sec and allowed to spin for about 15 seconds. The wafer rotation is then stoppedFIG. 5 is a chart illustrating thickness of a TARC layer applied to hydrophobic surface versus the volume of TARC used to form the layer according to the control method of FIG. 3. In FIG. 5, the volume of TARC indicated was applied to several wafers using the control method illustrated in FIG. 3 and described *supra*. A TARC volume of 5 ml is the nominal vol-



ume. It is readily seen that a minimum volume of about 2 ml of TARC is required to obtain a thickness close to a target thickness of about 650 Å. However, at a volume of 2 ml of TARC, many area of de-wets (no TARC coverage) are seen so in reality a minimum of 3ml of TARC is required for a de-wet free coating. Note, the standard deviation of the TARC thickness becomes unacceptable at volumes of about 4.0 ml or less.

[0037] FIG. 6 is a chart illustrating thickness of a TARC layer applied to hydrophobic surface versus the volume of TARC used to form the layer according to the method of the present invention of FIG. 4. The method of the present invention is referred to as the water pretreatment process on several occasions hereafter. In FIG. 6, the volume of TARC indicated was applied to several wafers using the method of the present invention illustrated in FIG. 4 and described *supra*. In FIG. 6, it is readily seen that a minimum volume of about 0.3 ml of TARC is required to obtain a thickness close to a target thickness of about 650 Å. In other studies a minimum volume of 0.15 ml of TARC was required to give a uniform thickness TARC layer. This is about 15% of the 2 ml minimum volume of TARC volume required for the control method and about 6% of the

5 ml nominal volume of TARC used in the control method. Note, the standard deviation of the TARC thickness remained acceptable down to a TARC dispense volume of about 0.3 ml in this study. In other studies the TARC dispense volume was about 0.15 ml.

[0038] FIG. 7 is a chart, illustrating image size control versus the volume of TARC applied according to the method of the present invention. In FIG. 7, both the top of a resist image and a bottom of the resist image at several positions on a wafer (several wafers per dispense volume) are plotted as well as the standard deviation of the measured linewidths. It can be readily seen that top and bottom image size remain nearly constant and the uniformity remains consistent with TARC dispense volumes as low as 0.3 ml. In other studies image size uniformity was obtained with a TARC dispense volume of 0.15 ml. Note, image sizes were measured on a commercially available critical dimension scanning electron microscopes (CD SEM) with edge detection/measurement software.

[0039] FIG. 8 is a chart comparing the control method and the method of the present invention to resist thickness versus the size of subsequently printed and developed images. In FIG. 8, image size versus resist thickness is plotted for

nominal control process of FIG. 3 (using a TARC dispense volume about 5 ml) and for the method of the present invention (TARC dispense volume about 0.5 ml) at a constant exposure energy. The chart of FIG. 8 shows that the method of the present invention did not significantly, if at all, alter the anti-reflective properties (i.e. index of refraction or TARC thickness) as there is little difference between the amplitudes of the control method and the water pre-treatment method. In addition there is very little difference in resist thickness.

[0040] It is possible for tool type and tool-to-tool differences of the water and TARC apply tool to affect the accuracy and repeatability of a process. TABLE III lists experimental measurements of TARC thickness and thickness standard deviation for the control process of FIG. 3 using techniques of a TARC dispense volume of 5 ml and the water pretreatment method of FIG. 4 using a TARC dispense volume of 0.5 ml, both techniques using TARC material AZ Aquatar (see TABLE II supra) various tools.

TABLE III

Tool	Control Mean Thickness (Å)	Control Wafer to Wafer Std Dev (Å)	Control within Wafer Std Dev (Å)	Water Pretreatment Mean Thickness (Å)	Water Pretreatment Wafer to Wafer Std Dev (Å)	Water Pretreatment within Wafer Std Dev (Å)
A	669	14.5	3.0	648	5.2	3.4
B	653	13.0	3.2	655	8.6	4.0
C	660	4.4	2.4	644	5.5	3.3
D	663	11.3	2.7	667	5.5	3.1
E	665	12.5	4.8	668	9.6	3.9

[0041] The data in TABLE III indicates that there is essentially no difference in TARC thickness or with wafer standard deviation between the control method and the method of the present invention and that the wafer to wafer standard deviation of the method of the present invention is superior to the wafer to wafer standard deviation of the control process for AZ Aquatar.

[0042] TABLE IV lists experimental measurements of TARC thickness and thickness standard deviation for the control process of FIG. 3 using techniques of a TARC dispense volume of 5 ml and the water pretreatment method of FIG. 4 using a TARC dispense volume of 0.3 ml, both techniques using TARC material JSR NFC-540 (see TABLE II supra).

TABLE IV

Tool	Control Mean Thickness (Å)	Control Wafer to Wafer Std Dev (Å)	Control within Wafer Std Dev (Å)	Water Pretreatment Mean Thickness (Å)	Water Pretreatment Wafer to Wafer Std Dev (Å)	Water Pretreatment within Wafer Std Dev (Å)
A	335	12.2	4.9	336	5.0	2.5
B	335	10.1	4.7	335	6.5	2.9
C	335	7.9	6.8	336	5.9	2.6

[0043] The data in TABLE IV indicates that there is essentially no difference in TARC thickness between the control method and the method of the present invention and that the uniformity (as measured by wafer to wafer and within wafer standard deviation) of the method of the present invention is superior to the uniformity of the control process for JSR NFC-540.

[0044] Thus, the present invention provides a method to reduce the amount of material required to form a uniform layer on a hydrophobic surface.

[0045] The description of the embodiments of the present invention is given above for the understanding of the present invention. It will be understood that the invention is not limited to the particular embodiments described herein, but is capable of various modifications, rearrangements and substitutions as will now become apparent to those skilled in the art without departing from the scope of the invention. For example, small quantities of additives such

as surfactants may be added to the water dispensed prior to TARC application. Therefore, it is intended that the following claims cover all such modifications and changes as fall within the true spirit and scope of the invention.